

High resolution molds, sacrificial in aqueous media, obtained by vat photopolymerization 3D printing

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ABSTRACT

From the synthesis of two methacrylic crosslinkers that contain in their structure β -amino esters activated for hydrolysis, photocurable formulations for vat photopolymerization have been prepared, in order to obtain sacrificial parts in aqueous media. Starting from binary formulations of both crosslinkers with the monofunctional monomer poly (ethylene glycol) methyl ether acrylate (PEGMEA), its printability has been demonstrated, as well as the sacrificial nature of the printed parts. Selecting a crosslinker weight percentage of 15%, optimization of the mechanical properties of the printed parts has been carried out through a variation of the formulation components, combining the crosslinker with 1 or 2 monofunctional monomers chosen from 2-hydroxy ethyl acrylate (HEA), PEGMEA, methacrylic acid (MAA) and 2-carboxyethyl acrylate (CEA), in different proportions. All the formulations were printable, and have allowed for modulating the mechanical properties of the printed parts, in terms of rigidity/flexibility and resistance. All printed parts have been shown to be sacrificial in basic water. Finally, a proof of concept has been carried out for its possible use as sacrificial molds, to obtain screws from a thermoplastic poly (ϵ -caprolactone) and from a silicone network, obtained respectively by heating and chemical crosslinking, followed by solubilisation in aqueous media.

1. Introduction

Additive manufacturing (AM), also known as 3D printing, is a major component of Industry 4.0 [1–4]. AM, benefiting from the rapid development of digital technologies [5], has become a key technology for fabricating customized products, due to its ability to create sophisticated objects with advanced attributes (new materials, geometries, shapes, mechanical, thermal and solubility properties) [2]. However, one of the major drawbacks of AM is still the limited materials selection portfolio, with low availability of high-performance materials with specific properties [6].

Among the wide variety of AM techniques, those based on vat photopolymerization processes, such as digital light projection (DLP), stereolithography (SLA) or liquid crystal display (LCD, also known as masked stereolithography, MSLA), offer the highest available resolution and are therefore the most extensively employed ones for high precision applications including jewelry [7], hearing aids [8], or in the dental sector [9], but also for the preparation of molds and tooling [10] just to

mention few of them.

DLP, LCD and SLA are vat photopolymerization printing techniques based on the use of UV-light to solidify a liquid resin layer-by-layer [3] but they differ in the light source: in DLP a projector is used to cure an entire layer at a time [11]. LCD uses the light from an array of LEDs masked by a LCD to form a 2D image of slices [4,12], and in contrast to the SLA laser [13], which must draw the entire layer to cure it [14]. As a result, in those cases where the fabrication of multiple parts is required or when the surface occupied by the part to be printed is large, LCD/DLP resulted to be significantly faster than SLA.

Currently, a myriad of SLA/LCD/DLP (vat photopolymerization) resins are available, which allow for printing materials with variable properties, ranging from elastic/flexible to tough or stable at high temperatures. However, as far as we know, there is a pending need to develop vat photopolymerization resins that enable the preparation of sacrificial parts, i.e. all the final models printed by vat photopolymerization results in non-reprocessable and non-soluble materials. In contrast to vat photopolymerization, this type of sacrificial materials

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has homologues in fused deposition modeling (FDM) (i.e., high impact polystyrene (HIPS) soluble in limonene and poly (vinyl alcohol) (PVA) soluble in water) [15,16] for the fabrication, for instance of supports or molds that need to be removed after use. However, the poor x-y resolution of FDM limited by the nozzle diameter (in the range of 200–400 μm) produce low quality molds in comparison to vat photopolymerization [17]. Therefore, taking into account the high precision of SLA/LCD/DLP, it would be highly desirable to provide resins that can be employed for the fabrication of high-resolution sacrificial molds. It is worth mentioning that currently those (non-sacrificial) molds made with SLA/LCD/DLP do not allow for the fabrication of intricate structures because they need to be integrally removed once the part has been fabricated. In this sense, sacrificial molds will significantly improve the complexity of the structures that could be produced.

Examples of crosslinker-free resins have been described, which, after vat photopolymerization, yield non-crosslinked pieces that could be used as sacrificial pieces since they can eventually be solubilized, for example, in water [18]. These examples are very unique and rare due to the fact that they are crosslinker-free, which on the one hand requires a very strict selection of the nature of the precursor (precursor of polymers poorly soluble in the monomer and with T_g well above ambient temperature) and printing parameters so that polymerization is very fast and high molecular weights are obtained in a short period of time. If all these requirements are not met the 3D printing process will fail and parts with adequate resolution could not be obtained or even no parts will be obtained at all. These requirements mean that this approach, although of great interest, is not very versatile and, for example, it is not possible to obtain molds with variable mechanical properties ranging from flexible to rigid.

Compared to the crosslinker-free systems described above, a sacrificial strategy focused on the use of crosslinkers would be much more versatile, since standard vat photopolymerization resins, including all commercial ones, contain crosslinking components. In fact, in most vat photopolymerization processes, a minimum amount of crosslinkers is required to obtain pieces with a suitable resolution and desirable mechanical properties. Indeed, vat photopolymerization resins are usually formulated with a high content of multifunctional crosslinkers to form stable non-swellable structures, that is, covalently linked polymer networks that remain unaltered during the lifetime of the 3D printed object. Based on these usual characteristics, it is explored here the design of sacrificial printed parts in SLA/LCD/DLP, i.e., the design and fabrication of 3D parts based on the use of labile crosslinkers. In this manner, the resin would comprise enough crosslinker for printing, with a minimum required for good definition and mechanical properties, but the printed part could be sacrificed by breaking the labile crosslinker's bridges and converting the polymer network into soluble chains. If the crosslinker is hydrolysable, like those used in this work, the printed part will be dissolved in water, a non-toxic and ubiquitous solvent, which is attractive toward its commercial implementation.

Based on our previous experience [19,20], in this work methacrylic crosslinkers containing hydrolysable β -amino esters were employed, which can satisfy the aforementioned needs.

2. Experimental section

2.1. Materials

PEGMEA (Mw 480), sodium hydroxide (NaOH), poly (ethylene glycol) dimethacrylate (PEGDMA550, Mw 550), 3-(acryloyloxy)–2-hydroxypropyl methacrylate, acetic acid, CEA, Sudan I and phenylbis (2,4,6-trimethyl benzoyl) phosphine oxide (PPO) were supplied by Sigma-Aldrich and used as received without further purification. Jeffamine ED-600 was supplied by Huntsman. HEA and MAA were supplied by TCI. 184 Silicone Elastomer Base and 184 Elastomer Curing Agent were supplied by Sylgard™. Poly (ϵ -caprolactone), (50.000 g mol^{-1}) (PCL) was supplied by Perstorp. All the chemicals were employed as

received unless specified.

2.2. Preparation and characterization of crosslinkers HCL1 and HCL2

3-(acryloyloxy)–2-hydroxypropyl methacrylate and diamino-containing structures (jeffamine to produce crosslinker HCL1 and piperazine to produce the crosslinker HCL2) were mixed in a 2:1 molar ratio. The reactions were carried out overnight at 37 °C in the presence of a catalytic amount of acetic acid (0.25 wt%). ^1H NMR spectroscopy was used to monitor the disappearance of acrylate signals as the reactions proceed. The compounds were used without ulterior purification.

^1H NMR HCL1 (400 MHz, CDCl_3) δ : 6.10 (m, 2 H, 1-H), 5.56 (m, 2 H, 1-H), 4.18 (m, 4 H 4-H), 3.92 (m, 2 H, 5-H), 3.80–3.17 (m, OH + 6-H + Hjeff), 3.03–2.69 (m, H- β + CHjeff), 2.50 (m, H- α + CH₂O), 1.92 (m, 6 H, Me), 1.11 (m, Me-jeff), 1.0 (m, Me-jeff) ppm.

^1H NMR HCL2 (400 MHz, CDCl_3) δ : 6.11 (m, 2 H, 1-H), 5.58 (m, 2 H, 1-H), 4.37–3.45 (m, 16 H, 4–6 H + OH + H- β), 2.80–2.37 (m, 12 H, 1'-H + 2'-H + H- α), 1.87 (m, 6 H, Me) ppm.

2.3. Formulations for 3D printing

For each resin or formulation, a total of 20 g of precursor mixture was prepared. Examples of each type of system are detailed below:

As an example of a resin from the HCL1 or HCL2 and PEGMEA (the resins were labeled as HCLn-XX, where n is 1 or 2, and XX is the weight percentage of HCL), formulation HCL1–30 was prepared by mixing 6 g of HCL1 and 14 g of PEGMEA.

As an example of resin from binary blends, the HCL1-HEA formulation was prepared by mixing 3 g of HCL1 and 17 g of HEA.

Finally, as an example of resin from the ternary blends, the formulation HCL1-HEA-CEA 60–25, which correspond to HCL1/HEA/CEA weight ratios of 15/60/25, was prepared by mixing 3 g of HCL1, 12 g of HEA and 5 g of CEA.

In all cases, 2.67 mg of Sudan I was added and the vessel was covered with aluminum foil to prevent from undesired polymerization. Then, 0.2 g (1 wt%) of photoinitiator was added and the mixture was stirred for 5–10 min until it was completely homogeneous. The resin was then ready to be tested in the printer.

2.4. 3D Printing

The resin was added into the tank and the following printing parameters were selected: layer height 100 μm , raft height 1 mm, raft offset 4 mm, layer exposure time 20 s, exposure off time 5 s, bottom layer exposure time 60 s, bottom layers 5 pcs, platform lower speed 100 mm/min and 5 platform lift speed 100 mm/min. The printer used was the Zortrax Inkspire using Z-Suite as slicer program. Creality LD-002 H (using Chitobox as slicer program) was used as secondary printer for first samples to demonstrate the universality of the resins.

After printing, a washing step in 2-propanol was carried out for 5 min and a post-curing process for 30 min at room temperature in a UV-curing chamber.

2.5. Solubilization tests

3D printed pieces ($2.0 \times 2.0 \times 0.2 \text{ cm}^3$) were immersed overnight in 15 mL of basic aqueous media (2 wt% NaOH) at room temperature. After this time, the solubilization of the piece was visually analyzed in order to observe the disappearance of the mold. The dissolved material of the mold was analyzed by ^1H NMR (see Figs. S1 and S2 in SI).

2.6. Use of 3D printed parts as sacrificial molds: proof of concept for the preparation of thermoplastic and silicon based parts

To carry out a proof of concept for the use of the printed parts as

sacrificial molds, two types of screw molds with different thread pitches (1 and 2 mm) were digitally designed (see Fig. S3 in SI) and printed. In both cases, the dimensions of the screw filler, were 1.5 cm of height and 1/2 cm of thread/head diameter.

Example 1. Sacrificial molds for the fabrication of 3D structures using thermoplastic polymers.

PCL pellets were introduced into the mold, and the construct was heated up to 100 °C until PCL was melted. Thereafter, the construct was allowed to cool down to room temperature for 1 h and subsequently immersed overnight in basic aqueous media. Finally, the 3D structured PCL part was recovered from the solution, surface dried and stored.

Example 2. Chemical crosslinking inside the sacrificial 3D printed molds: Fabrication of silicone networks.

The silicone based elastomeric kit Sylgard 184, is a liquid two-component system: 1) a polymer (named base) 2) and a curing agent that cross-links with the base, were used. Both components 1) polymer (base) and 2) curing agent, were mixed in a 10:1 (base:curing agent) ratio by weight. The mixture was stirred manually and left under vacuum for 15 min to avoid contact with the entrapped oxygen. The mixture was then added to the printed sacrificial molds and placed in the oven at 60°C overnight to form the crosslinked silicon elastomer. Later, the construct (mold with the cured Sylgard 184) was immersed overnight in basic water. Finally, the silicone network was recovered from the solution, dried and stored.

2.7. Characterization methods

Rheological characterization of the uncured formulations was carried out at 25 °C using a strain-controlled rheometer (Waters, ARG2, TA Instruments) with a cone and plate geometry (40 mm diameter). The viscosity was measured at a shear rate between 0.3 and 100 s⁻¹. For every resin, three viscosity measurements were performed to confirm the reproducibility of the measurements.

¹H NMR spectra were recorded at room temperature in a Bruker 400 instrument using chloroform (CDCl₃) as the solvent for HCL1 and HCL2, and D₂O for the analysis of the product resulting from the solubilization tests.

Attenuated total reflectance-infrared spectroscopy (ATR-FTIR) was conducted on dried samples using a FT-IR Spectrometer (Spectrum Two) from PerkinElmer, equipped with a diamond crystal ATR accessory. Spectra were recorded with a resolution of 4 cm⁻¹ in the range of 4000–500 cm⁻¹ for each sample.

Thermal analyses were carried out in a thermogravimetric analyzer (TGA) controlled by METTLER instrument. 10 mg of powdered sample was heated from 0 up to 800 °C. The experiments were performed under oxygen flow, using a slow temperature increment (10°C/min).

Scanning electron microscopy (SEM) measurements were performed using a XL30 ESEM (Phillips), at an acceleration voltage of 25 kV.

Dimensional accuracy analysis of cylinders was carried out by measuring dimensions (diameter and height) with a micrometer. In the case of screws, imageJ was used to analyze photographs of representative screw molds.

2.8. Mechanical testing

Two types of mechanical tests were carried out, compression tests and tensile strength tests. Measurements were carried out in a "Universal testing machine", INSTRON brand, with Load cells of 100 N, 1 kN and 5 kN, depending on the need, tensile test speed: 100 mm/min and compression test speed: 10 mm/min.

The size of the compression specimens (always 5 specimens for each test) was 29 cm in diameter and 12.5 cm in height. 4 sweeps were run until 25% of deformation of the pieces, following the RevUNE 53536.

The size of the tensile test pieces (5 pieces for each test) was V test

type of the ASTM D638–14 (Standard Test Method for Tensile Properties of Plastics), that is, W (Width of narrow section) = 3.18 ± 0.03 mm (0.125 ± 0.001 in.), L (Length of narrow section) = 9.53 ± 0.08 mm (0.375 ± 0.003 in.), G (Gage length) = 7.62 ± 0.02 mm (0.300 ± 0.001 in.), and R (Radius of fillet) = 12.7 ± 0.08 mm (0.500 ± 0.003 in.).

3. Results and discussion

This strategy employed to fabricate 3D printed pieces (sacrificial in aqueous media) is illustrated in Fig. 1 using representative structures of the components used in the formulations of the photopolymerizable resins developed in this work. In this study, the key components are a hydrolysable crosslinker such as HCL1, carrying a jeffamine-derived spacer and β-amino ester bonds activated for hydrolysis, and hydrophilic monofunctional monomers (in this case PEGMEA) that allows for tuning the characteristics of the resin and, in turn, of the printed piece and eventually of the hydrolytic process.

3.1. Synthesis of hydrolysable crosslinkers

A generic route to obtain methacrylates bearing hydrolysable side chains by means of a Michael addition of amines on asymmetric acrylic structures comprising simultaneously methacrylate and acrylate groups has been previously reported by our group [19,20]. This route takes advantage of the very high selectivity of the reaction towards the acrylate group. The obtained methacrylates bear β-amino ester groups in their side chain, which are known to have a high activation towards hydrolysis [21,22]. A similar route was devised in this work, to obtain a dimethacrylate containing β-amino esters in the spacer moiety, by Michael addition of diamines to 3-(acryloyloxy)–2-hydroxypropyl methacrylate (also called 1-(acryloyloxy)–3-(methacryloyloxy)–2-propanol), (1), as asymmetric structure, in a 1:2 molar ratio. Diamines only react with the acrylate group. This route has been previously described to prepare crosslinkers for different applications (not for 3D printing purposes, not for sacrificial purposes)[23–26]. Jeffamine ED-600 (2) and piperazine (3) were selected as diamines, to obtain the structures shown in Fig. 2, what are denoted as HCL1 and HCL2 (HCLs, stands for hydrolysable crosslinkers).

This reaction proceeded quantitatively, from relatively cheap commercial chemicals, and without the use of solvents allowing for the use of the reaction product, with no need for further purification. These characteristics of the reaction make them very promising for future scalability purposes in resin preparation.

3.2. Initial tests and adjustments using HCL-PEGMEA binary system

To impart versatility to the range of final properties, the photocurable resin can be formulated by incorporating, in addition to HCL, other monofunctional monomers in different weight ratios. Properties such as the resin viscosity, mechanical properties of the printed part or water solubility after hydrolysis, can be modulated by a correct choice of these components, as well as the weight ratio of the different precursors. Taking into account that many of the commercial LCD/DLP resins use precursors derived from poly ethylene glycol (PEG) such as PEG-based acrylates or crosslinkers [27,28], poly (ethylene glycol) methyl ether acrylate (M_n 480), PEGMEA, has been initially selected as monofunctional monomer, to be combined with HCLs in different HCL/PEGMEA weight ratios. It should be noted that jeffamine is a PEG-related structure. In the context of our design, PEG-based chain segments will ensure negligible toxicity and will favor the solubility in water of the final residual chains. It must be noted that, after photopolymerization and the formation of the polymerized crosslinked solid part, the hydrolysis of the two synthesized crosslinkers yield glycerol methacrylate type units (see final blue structure in Fig. 1).

Formulations with different HCL/PEGMEA weight ratios were prepared, and the influence of this composition ratio on the printability and

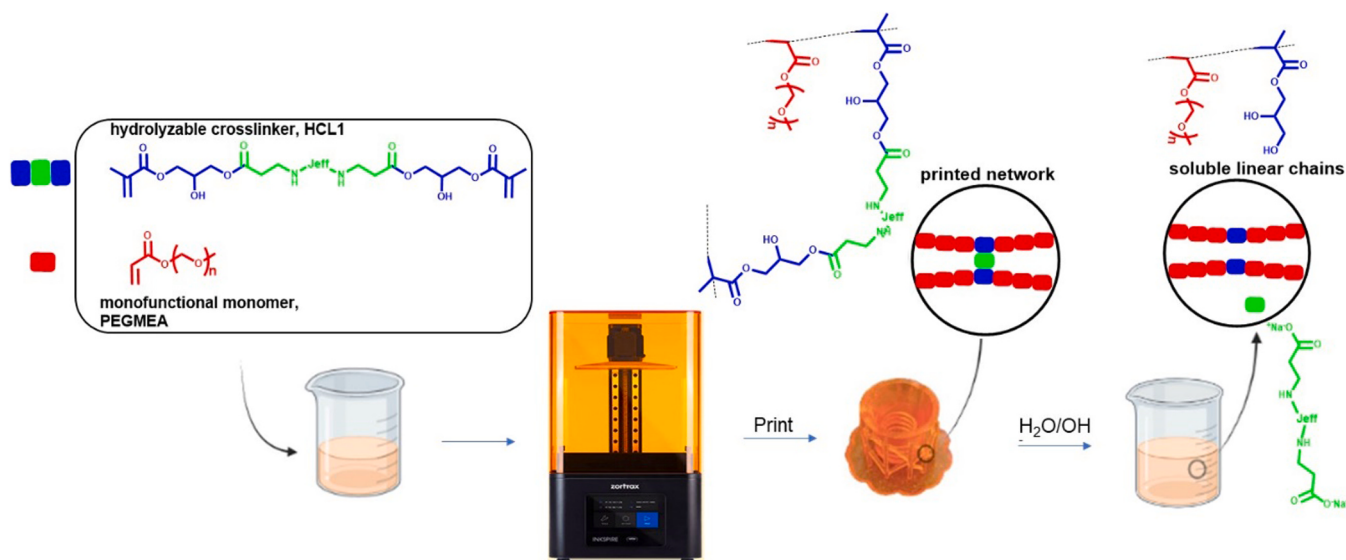


Fig. 1. Strategy to prepare sacrificial (in water) 3D printable polymeric materials from resins containing HCL1 as hydrolysable crosslinker and PEGMEA as monofunctional monomer. After polymerization (3D printing), a polymer network is obtained, which is sacrificial in basic water because the crosslinking bridges are hydrolysable thus leading to soluble linear chains.

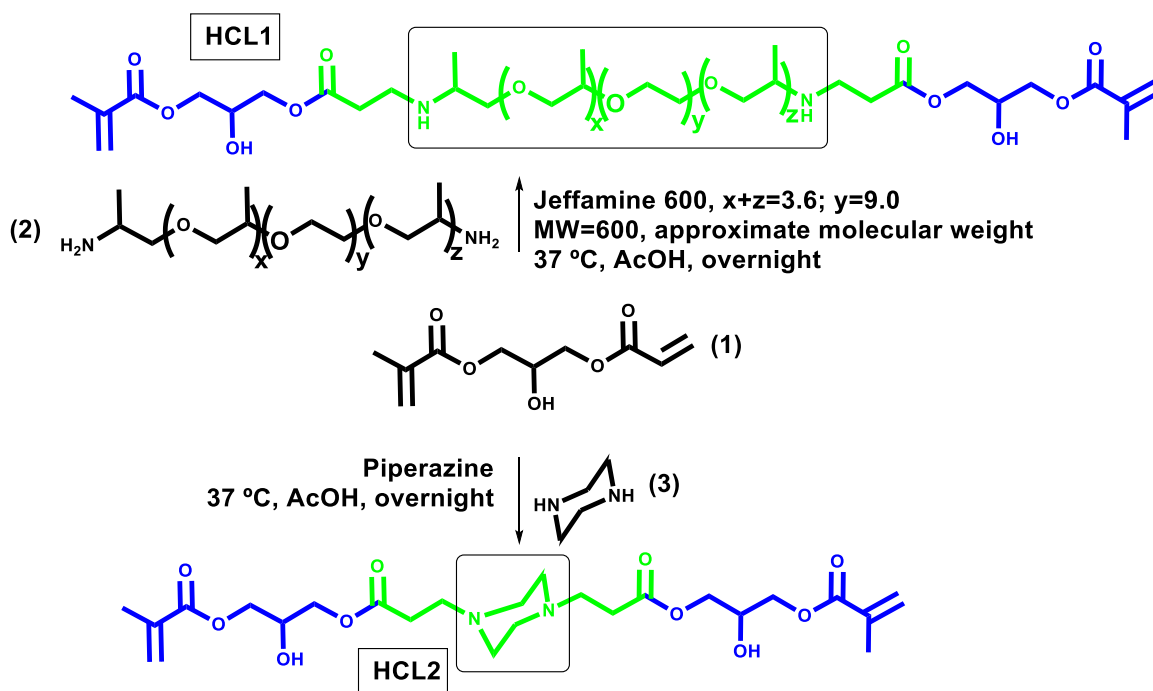


Fig. 2. Synthetic procedure to obtain the hydrolysable crosslinkers HCL1 and HCL2, by using two different diamines. The colors in this figure are related to Fig. 1.

properties of the printed pieces was studied. The resins have been labeled as HCLn-XX, with n being 1 or 2, and XX the weight percentage of HCLn in the formulation of the photopolymerizable resin.

3.2.1. Printability of HCL-PEGMEA resins

In a first series of experiments, a rheological study was carried out to measure the viscosity as a function of the shear rate, which is summarized in Fig. S4 in SI. Although all the resins showed a Newtonian behavior, it was observed that an increasing proportion of HCLn in the mixture produces photopolymerizable resins with higher viscosity. Particularly interesting is the resin comprising exclusively HCL where the viscosity of HCL2-100 is more than an order of magnitude higher than that of HCL1-100. Representative viscosity values obtained for a

shear rate of 1 s^{-1} are depicted in Fig. 3. Low viscosities are known to be required for SLA/LCD/DLP printing [14,29]. Within the exception of both HCLn100 systems (HCL1-100 and HCL2-100) and HCL2-75, the viscosities of the resins were determined to be less than $1 \text{ Pa}\cdot\text{s}$. Resins with lower ratios of HCL have viscosities close to or even less than $0.1 \text{ Pa}\cdot\text{s}$, which are highly suitable values for DLP/LCD printing [30].

In summary, resins with HCL weight percentages of 45 and lower presented appropriated viscosities for printing. In view of these results, and the interest in using the lowest possible amount of HCL in the formulation of the resin for scaling, printability and characterization tests of the printed pieces, this study was carried out with photopolymerizable resins with HCL wt% of 45 or lower. It is worth mentioning that a minimum of 20 s of exposure time in each layer was

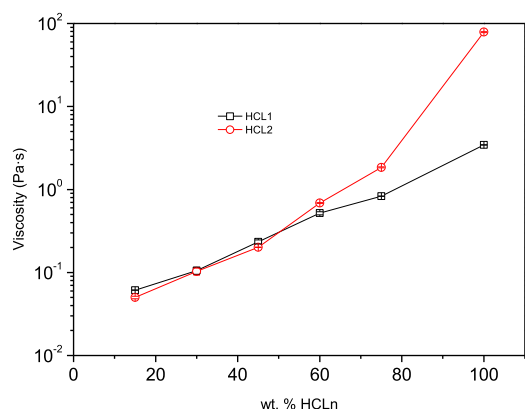


Fig. 3. Viscosity values for a shear rate of 1 s^{-1} for the different HCLn/PEGMEA ratios. Error bars are contained inside the symbols.

required to allow for the photopolymerization to proceed in order to ensure the correct anchoring of the 3D printed part onto the fabrication platform. Printability of each resin was tested using a rather simple printing design ($2.0 \times 2.0 \times 0.2 \text{ cm}^3$, see Fig. S5 in SI). According to previous studies, the photoabsorber Sudan was added at 1.35 wt%, to limit the UV-light penetration [31]. In those cases where Sudan was not used, pieces with a poorer resolution were obtained (see Fig. S6 in SI). The optimized printing parameters are described in the Experimental Section. As mentioned in this Section, the Zortrax Inkspire (LCD 3D printer) was used, but in the first tests it was found that with other LCD 3D printers such as the Creality LD-002 H and LD002-R the same result was achieved, confirming the universality of the resin.

From these experiments, it could be concluded that the minimum amount of HCL necessary for DLP/LCD printing with these resins, to achieve minimum printability and workability, was 15 wt% (pieces were not correctly formed below this content). This cutoff percentage is in good agreement with other previous studies [2,32–35]. The rest of the resins with percentages of HCL higher than 15% by weight could be properly printed.

In addition to the amount of crosslinking, another critical aspect is to

check the complete light-curing of the resin after 3D printing and whether a post-curing step is necessary for this. To address this aspect FT-IR analysis were carried out (Fig. S7 in SI) for the resin and a printed and post-cured piece (30 min, r.t.). As can be observed, the signals of the polymerizable double bonds within the interval $1675\text{--}1600 \text{ cm}^{-1}$ range disappear, which confirms the complete polymerization of the resin upon post-curing.

3.2.2. Properties of parts printed using HCL-PEGMEA resins

The sacrificial character of these 3D printed samples obtained in dimensions $2.0 \times 2.0 \times 0.2 \text{ cm}^3$ was preliminarily tested by immersing them in aqueous basic medium (NaOH 2 wt%). In all cases, the samples were solubilized overnight at room temperature. The solubilized structures were characterized by proton NMR spectroscopy. The spectrum obtained was consistent with the proposed mechanism (see SI and Figs. S1 and S2). A reference network prepared by substituting HCL1 by the stable crosslinker PEGDMA did not solubilize after 24 h, but instead became a swollen network (See Fig. S8 in SI).

Provided the fabrication conditions as well as the solubility of the resin in basic conditions, the printed parts obtained from these resins were mechanically characterized by both tensile and compression tests (photographs of the specimens are shown in Fig. 4 and Fig. S5 in SI). Table 1 shows the mechanical characteristics of the 3D printed materials obtained using both crosslinking agents. According to the results summarized in Table 1 and Fig. 4, the higher the amount of HCL the higher the strength, being the HCL2 system less brittle than the HCL1 one. For both families, the higher the HCL content, the higher the modulus, although low values can be considered (in the interval of 1–16 MPa). It is observed that, for the same HCL wt%, the HCL2 family shows a higher modulus (both Young's and compression) than the HCL1 family. Most probably, this difference is related to the fact that HCL1, being longer (higher molar mass) than HCL2, leads to less molar crosslinking density than HCL2 for photopolymerizable resins with a similar weight percentage. It is interesting to note that when comparing systems of both families with similar molar crosslinking, the moduli are closer (i.e., HCL1–30 as compared to HCL2–15, or HCL1–45 as compared to HCL2–30, see Table 1). 3D printed parts using both crosslinking agents are rather brittle, showing values of deformation at break, in tension

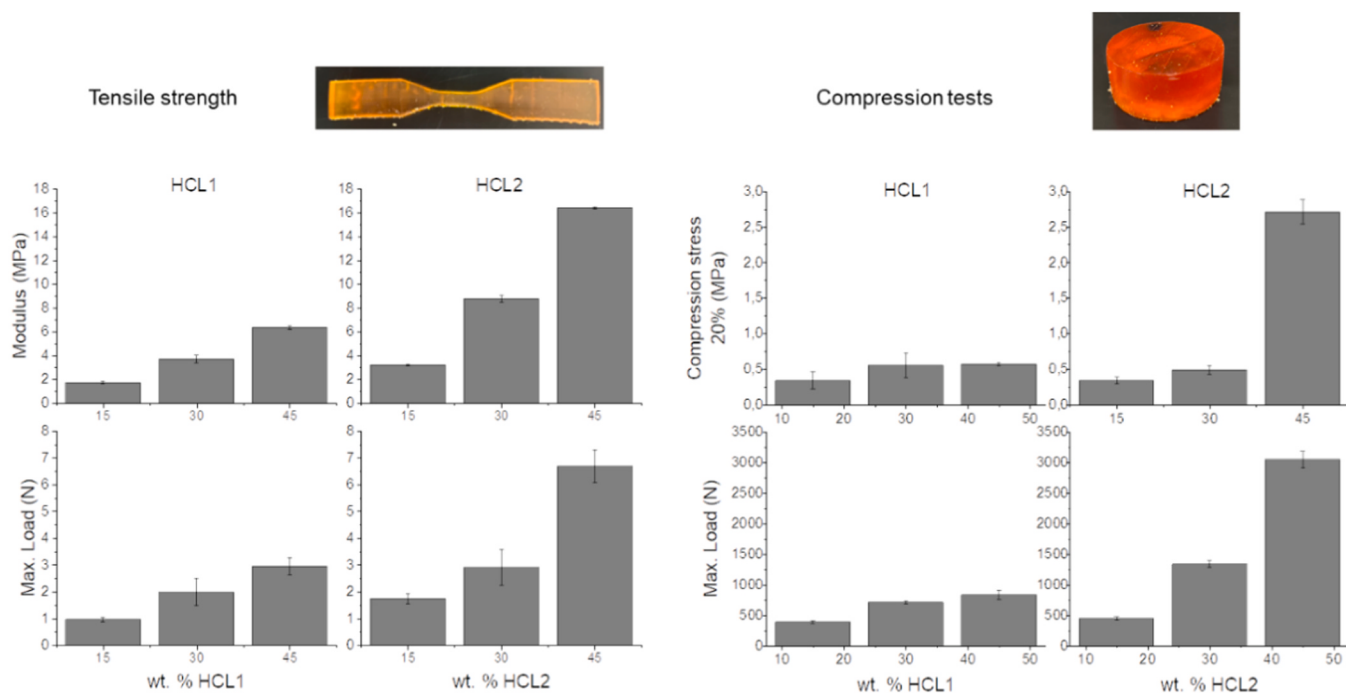


Fig. 4. Tensile and compression results of HCLn-XX as a function of the HCLn content in the resin.

Table 1

Data of the HCLn-XX systems. Data are plotted in Fig. 4.

Label	HCL %		Tension			Compression			Sacrificial?a)
	Wt.	Mol	E (MPa)	Strain break (%)	Maximum Load (N)	K (MPa)	Compression stress (MPa) 20%	Maximum Load (N)	
HCL1									
HCL1-15 **	15	7.5	1.74 ± 0.09	5.78 ± 0.49	0.97 ± 0.07	1.61 ± 0.09	0.34 ± 0.12	393 ± 19	Yes
HCL1-30 **	30	16.7	3.72 ± 0.31	5.54 ± 0.52	2.00 ± 0.51	4.36 ± 0.12	0.55 ± 0.17	662 ± 37	Yes
HCL1-45	45	27.6	6.35 ± 0.16	5.70 ± 0.44	2.95 ± 0.31	5.41 ± 0.40	0.57 ± 0.02	937 ± 5	Yes
HCL2									
HCL2-15 **	15	14.1	3.21 ± 0.08	6.30 ± 0.42	1.75 ± 0.18	2.77 ± 0.16	0.34 ± 0.05	449 ± 29	Yes
HCL2-30 *	30	28.6	8.78 ± 0.26	4.33 ± 0.34	2.91 ± 0.67	6.28 ± 0.25	0.49 ± 0.06	1342 ± 51	Yes
HCL2-45	45	43.3	16.4 ± 0.05	5.73 ± 0.63	6.68 ± 0.60	16.4 ± 0.7	2.71 ± 0.17	3051 ± 141	Yes

a) Immersion in basic aqueous media (NaOH 2 wt%). All samples were solubilized overnight.

* Successfully tested as molds to prepare PCL screws (according to Section 3.5).

** Successfully tested as molds to prepare PCL and silicone screws (according to Section 3.5).

tests, in the order of 5%. The values of stress at break are higher in the HCL2-PEGMEA system, and in both cases, it increases with the amount of HCL, which is in good agreement with the results obtained in the tensile strength tests. The compression measurements, recorded up to 25% of deformation, also ended up breaking the tested 3D printed specimens. In any case, the HCL2 based 3D printed parts were slightly stronger than those prepared using HCL1, and required higher loads to break as shown in Fig. 4 and summarized in Table 1.

3.3. Study of other HCL-based systems. Modulation of properties of the printed parts

The HCL-PEGMEA systems studied in the previous section have shown to be perfectly printable, although the printed parts showed low moduli (they exhibited some flexibility) and limited deformation before breaking. An optimization of the properties of the printed parts was addressed through the evaluation of other monofunctional monomers and combinations of them. For this purpose, HCL1 was selected as crosslinking agent and in a fixed wt. percentage of 15% (minimum crosslinking required for printability). It is worth mentioning that a lower content of HCL1 will favour subsequent hydrolysis since the system will swell to a higher extent and the crosslinking density will be lower. HCL1 was chosen because the properties of HCL1-15 and HCL2-15 are similar.

As alternative monofunctional monomers to PEGMEA the selected monomers were: HEA, CEA and MAA (see structures in Fig. 5). A study on the preparation of resins with 15 wt% HCL1 and different combinations of HEA, CEA and/or MAA has been carried out in two stages: binary and ternary formulations, that is, first analysing the effect of each monomer separately and secondly evidencing the possibility of

modulating the properties by using mixtures of two different monofunctional monomers.

3.3.1. HCL-based binary systems

In a first series of experiments, binary resins were prepared containing, in addition to 15 wt% of HCL1, one of the four selected monomers. These binary systems were labelled as HCL1-PEGMEA, HCL1-HEA, HCL1-CEA, and HCL1-MAA. HEA was selected as a low molecular weight model of PEGMEA, for two reasons: on one hand, for the selected fixed HCL1 content of 15 wt%, the monofunctional monomer size will define the crosslinking molar density, i.e., monomers with higher molar masses will result in higher crosslinking molar density. Thus, the HCL1/PEGMEA and HCL1/HEA molar ratios are respectively 7.5 and 1.9. This difference is liable to have a great influence on the properties of the printed parts, as already indicated by the comparative analysis of HCL1 and HCL2 described in Section 3.2. On the other hand, HEA, compared to PEGMEA, leads to polymer chains with a higher glass transition temperature (Tg). Thus, the Tg of PEG-(meth)acrylate type homopolymers has been reported to be around -70 °C (which is in agreement with the flexible nature of the HCL1-PEGMEA samples) [36], whereas that of poly-HEA is around -2 °C [37,38]. Therefore, CEA and MAA were selected as precursor monomers for polymers with higher Tg values of 30 and 228 °C, respectively [39]. Therefore, a range of polymer precursors with increasing values of Tg was employed in this study. It was expected that the rigidity and strength of the printed parts can be controlled with this selection. Furthermore, CEA and MAA are ionizable moieties and are expected to facilitate the sacrifice process (swelling and hydrolysis).

3.3.1.1. Printability of HCL-based binary resins. Once the rationale behind the selection of the monomers was provided, the resins were rheologically evaluated to analyse whether the viscosities of the resins remain suitable for printing when exchanging PEGMEA by other monomers. Fig. 5 shows the viscosity values as a function of the shear rate for the 4 systems. It is observed that all the photopolymerizable mixtures have Newtonian behaviours and, except for the HCL1-CEA system, presented viscosities below 0.1 Pa·s. The viscosity of the HCL1-CEA system, though somewhat higher (close to 0.5 Pa·s), also proved suitable for printing.

3.3.1.2. Properties of parts printed using HCL-based binary resins. All formulations could be printed using the conditions selected in Section 3.2. and the resulting 3D printed parts could be solubilized overnight at room temperature in basic aqueous media. For the mechanical characterization of the resulting printed materials, specimen for compression and tensile tests were printed and evaluated (see Fig. S5 in SI). The simple handling of the parts already showed clear differences: the HCL1-PEGMEA system, as described above, gave rise to somewhat brittle printed parts. Moreover, as will be discussed, the 3D printed parts

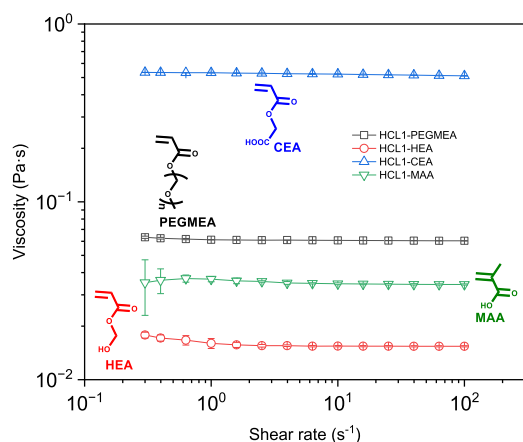


Fig. 5. Viscosity values as a function of shear rate for the HCL1-PEGMEA, HCL1-HEA, HCL1-CEA and HCL1-MAA resins.

containing HEA and CEA exhibited improved mechanical properties. As a result, stronger, either elastic or flexible printed parts with different degrees of strength (CEA derivatives stronger than HEA derivatives) (Fig. 6) can be obtained from the HEA and CEA systems. Systems containing MAA gave rise to very rigid parts. These differences in the mechanical values are shown in Fig. 6 and Table S1 in SI. The Young's and compression modulus of the pieces obtained from the resins containing PEGMEA and HEA are one or two orders of magnitude lower than those of the pieces obtained with resins containing CEA and MAA, respectively. The strain at break (%) data of the elastic HCL1-HEA systems are much higher than those obtained with the HCL1-PEGMEA pieces, which is in accordance with the greater fragility of these last pieces. Systems containing HEA give rise to pieces with higher modulus and less brittleness than pieces containing PEGMEA, what can be associated to the difference in crosslinking molar density, which is more than three times higher for the HCL1-PEGMEA system than for HCL1-HEA. The pieces of the HCL1-CEA system, which are also elastic, have even higher strain at break values (~142%) for maximum load than HCL1-HEA (~38%). The parts of the HCL1-MAA system hardly deform before breaking at higher loads than any other system, which is indicative of the aforementioned high rigidity. Compression data at 20% deformation for the HCL1-CEA and HCL1-MAA systems were not included because the maximum load of the apparatus (5000 N) was reached before reaching that percentage of deformation.

Since the systems are intended to be used as sacrificial molds, it is interesting to analyse the thermal stability of the 3D printed parts, so that a thermal range can be established for a specific application. Printed samples were characterized by TGA. From the thermograms (Fig. 7), the values of $T_{5\%}$, that is, the temperature at which the sample has lost 5% of its mass, were determined and collected in Table S1 in SI. This temperature has been used as the temperature where degradation begins. It can be seen that all the systems remain stable up to ~180 °C with some differences depending on the employed monomer. Whereas the HCL1-CEA system can be used below 183 °C. The other systems can be used at temperatures around 200 °C for HCL1-PEGMEA and up to 220 °C for HCL1-HEA and HCL1-MAA (see Table S1 in SI).

3.3.2. HCL-based ternary systems

The study of binary systems depicted above evidenced that the mechanical properties of the printed parts can be modulated, at least to a certain extent, by combining HCL1 with different monofunctional monomers with variable side chain lengths and hydrophilicity/charge. As described above, printed parts with Young's modulus of 1.74, 2.59, 121 and 2200 MPa were obtained by using photopolymerizable resins comprising HCL1 and PEGMEA, HEA, CEA and MAA respectively. Whereas the parts fabricated using PEGMEA were fragile, those obtained with MAA were very rigid. Moreover, the HEA and CEA systems made it possible to print robust parts with different degrees of flexibility (the HEA system being more flexible than the CEA system). In this context, more continuous or finer modulation of properties can be achieved by

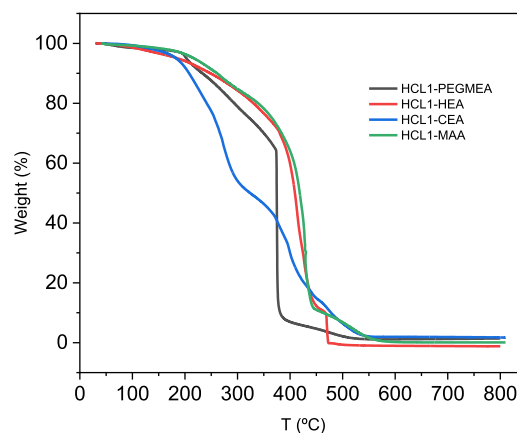


Fig. 7. Thermograms of the different binary systems investigated using HCL1 as crosslinking agent and the monomers PEGMEA, HEA, CEA and MAA.

using ternary systems, i.e., HCL1 (fixed at 15 wt%) and dual combinations of the four monofunctional monomers in different ratios. For clarity purposes, the possible combinations have been restricted to HEA-based ternary systems, i.e., HCL1-HEA-PEGMEA, HCL1-HEA-CEA, and HCL1-HEA-MAA, with different wt% of HEA and the third component (see Table S2 in SI). This choice has been made because HCL1-HEA is the binary resin with lowest viscosity (see Fig. 5), and due to the contribution of HEA to the thermal stability, robustness and flexibility, as well as to its homology with PEGMEA. Thus, in systems with CEA and MAA, it is expected that the ternary combinations will lead to parts with gradual Young modulus from highly rigid systems with only MAA to highly flexible and robust systems with only HEA, through systems with intermediate flexibility and very robust with only CEA. The PEGMEA system has been included for comparative purposes.

The ternary systems have been therefore labeled as HCL1-HEA-Z XX-YY, where Z is PEGMEA, CEA or MAA, and XX and YY are the weight percentages of HEA and Z respectively ($XX+YY=85$).

3.3.2.1. Printability of HCL-based ternary resins. The rheological study confirmed that all the ternary resins show a Newtonian behaviour, and that the viscosity values are intermediate between the values of the binary systems, being dependent on the composition (see Fig. 8). Of interest is the variation of the viscosity in the system HCL1-HEA-CEA, from 0.5 Pa·s. of the resin with only CEA (HCL1-CEA) to values close to 0.01 of the system made of only HEA (HCL1-HEA; please note that the Y-axis is displayed as a logarithmic scale). Taking into account the background of the study of binary systems (Section 3.3.1), it has therefore been considered that all resins have appropriate viscosities for printing. This was in fact confirmed by printing all of them into stable pieces ($2.0 \times 2.0 \times 0.2 \text{ cm}^3$). It also should be mentioned that the explored compositions did not significantly affect the solubilization process and,

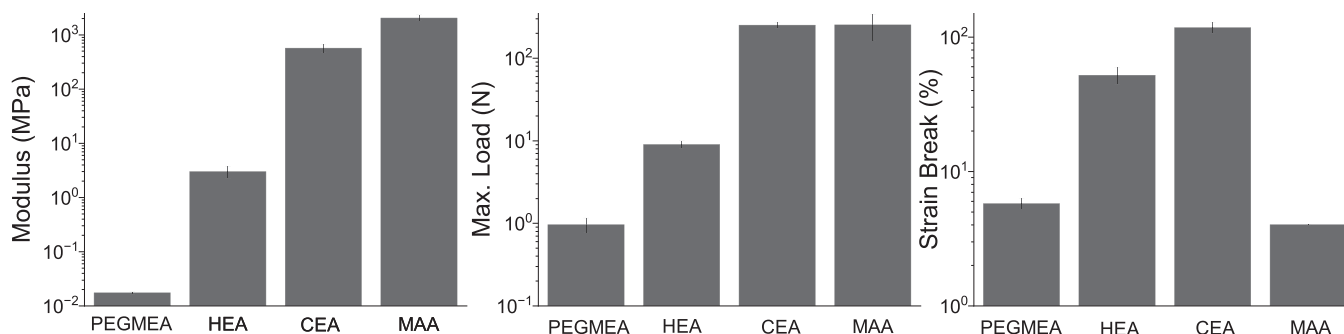


Fig. 6. Mechanical characteristics of the 3D printed specimen resulting from tensile-strain tests for the following systems: HCL1-PEGMEA, HCL1-HEA, HCL1-CEA and HCL1-MAA.

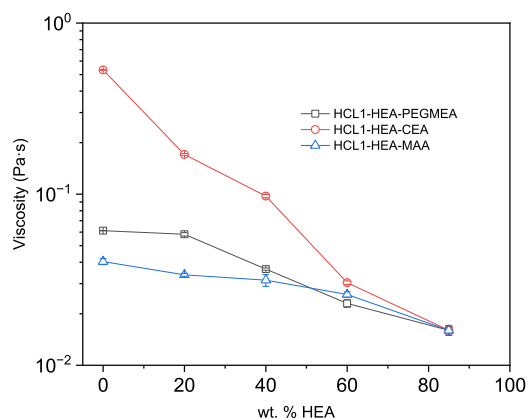


Fig. 8. Viscosity values for a shear rate of 1 s^{-1} for the different resins. Please note that the wt% of HCL is always 15%.

therefore, all samples were solubilized overnight at room temperature in basic aqueous media.

3.3.2.2. Properties of parts printed using HCL-based ternary resins. The 3D

printed parts obtained with the different systems were thermally and mechanically characterized by TGA, tensile and compression tests respectively (specimen were prepared according to the Experimental Section and Fig. S5 in SI). The mechanical properties of the different systems obtained from the tensile-strain tests have been depicted in Fig. 9. Upon thoroughly analysing system by system, it is possible to evidence that in HCL1-HEA-PEGMEA an increase in the flexibility of the printed materials is observed in the photopolymerizable resins with higher HEA content. As described before, the HCL1-PEGMEA binary system is very brittle, breaking at 5% strains with very low load (0.97 N), while HCL1-HEA is significantly more flexible and elastic, breaking at 38% strain and under load one order of magnitude higher (9 N, also low). Systems with both components show intermediate and compositionally correlative properties, being the compositions close to HCL1-HEA eligible for their use as molds according to their resistance. The differences associated with the composition must be ascribed, at least in part, to the change in the molar crosslinking density, which progressively decreases with increasing amount of HEA. Regarding thermal stability (Figs. S9, S10 and S11 in SI), ternary systems have shown significantly higher stability than the binary controls, and can be used up to temperatures of 260–270 °C. This unexpected increase in the thermal resistance still requires further investigation but nevertheless will allow for their use in a larger range of temperatures.

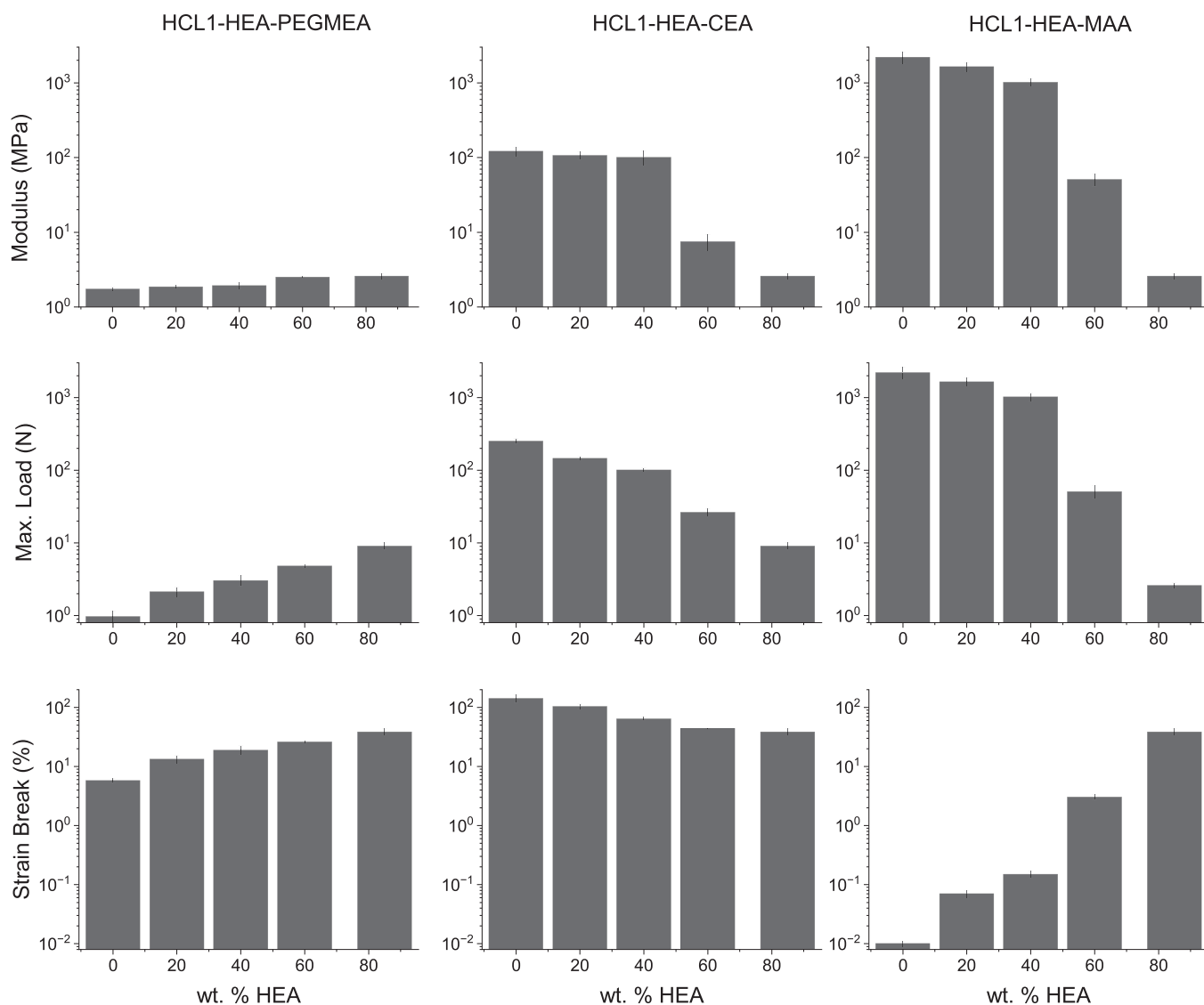


Fig. 9. Parameters from tensile tests of ternary systems as function of the HEA content.

The HCL1-HEA-CEA system is flexible and elastic in all compositions. Nevertheless, an increase in the molar amount of CEA produced parts with improved modulus, improved deformation capacity before breaking (it is more elastomeric) and, therefore, the load at break increases.[40] Intermediate compositions have intermediate properties correlated with the composition. The thermal stability of these series of resins presented maximum temperatures of use of around 190 °C.

Finally, 3D printed parts fabricated from HCL1-HEA-MAA ternary photopolymerizable resins were, in comparison with the previous systems, rather rigid. More precisely, moduli of the parts were - independently of the compositions- near the binary control HCL1-MAA and above 1 GPa. These materials are brittle, they break at minimal deformations, although they require very high loads to do so. The thermal stability is similar to the binary controls.

A global analysis indicates that it is possible to modulate the mechanical properties of printed parts, from elastic and highly flexible parts (HCL1-HEA-CEA system), to very rigid parts (MAA-rich formulations in the HCL1-HEA-CEA system), and therefore robust flexible and rigid parts can be manufactured. All materials can be used at temperatures below 180 °C. If higher temperatures are required, there are options to select materials with ranges of use up to 270 °C.

3.4. Dimensional accuracy analysis

We have carried out dimensional measurements on cylinder type representative samples, printed from the digital design mentioned in Table S3 in SI. The measurements have been made in triplicate. It can be seen that in most cases, the dimensional accuracy is excellent. Only in the pieces that contain CEA is a small deviation observed. This behavior may be related to the measurement method and the high elasticity of CEA derivatives, which may make the measurement less reliable.

3.5. Proof of concept for the use of sacrificial molds

Provided an adequate printability and sacrificial nature (based on their hydrolysis and solubility in basic aqueous solutions) of all the systems described in the previous sections, selected formulations were used for the preparation of sacrificial molds. SLA/LCD/DLP are without any doubt the current commercially available technology with the best resolution and different sectors ranging from dentistry to jewellery

employ this technology for the fabrication of molds. In this sense, for some particular applications where mold removal supposes a challenge such as those parts with intricate internal structures or with delicate surface patterns, the use of soluble molds could be an interesting alternative.

For this proof of concept, a mold with an internal screw shape was selected (mold designs are described in the Experimental Section). To test dimensional accuracy on these samples, the thread pitches of three printed screws have been analyzed for representative formulations (Fig. S12 in SI), obtaining values very close to those of the digital design (these measurements have been included in Table S3 in SI).

More interestingly, to test the versatility of these fabricated molds two different materials that require different processing methods were evaluated. On the one hand, rigid screws of a thermoplastic polymer able to melt and flow into the mold were prepared. As thermoplastic polymer PCL was selected. PCL is a semicrystalline polymer, biocompatible, FDA approved and extensively used for biomedical applications. The mold was filled with solid PCL pellets, heated at 100 °C for the time necessary for the molten polymer to completely fill the mold, after which it was allowed to cool to room temperature. Finally, the screw-shaped PCL was recovered by complete solubilization of the resin in basic conditions overnight. It is worth mentioning that PCL upon melting decreases significantly the viscosity and, as depicted in Fig. 10, was able to completely fill the mold.

On the other hand, reactive processable materials were equally explored. More precisely, elastic silicone screws prepared by filling the mold with the commercial liquid two-component formulation Sylgard 184, followed by overnight curing at 60 °C. Similar to the example depicted above the silicon-based screws were recovered by overnight immersion in a basic aqueous medium (Fig. 10).

These preparative processes, selected to evidence the potential of these materials, have been evaluated with representative samples of the three families described above. The selected compositions have been indicated in Table 1, S1 and S2 (in SI) with one or two asterisks (indicating whether it has only been used in the preparation of PCL screws or if it has been used to obtain screws of both types, respectively). Interestingly, in all cases the fabrication of the desired part was successfully achieved, that is, in all cases the conditions employed for the preparation (temperature and time) did not alter the 3D printed structure and, upon immersion in basic aqueous solution, the mold could be

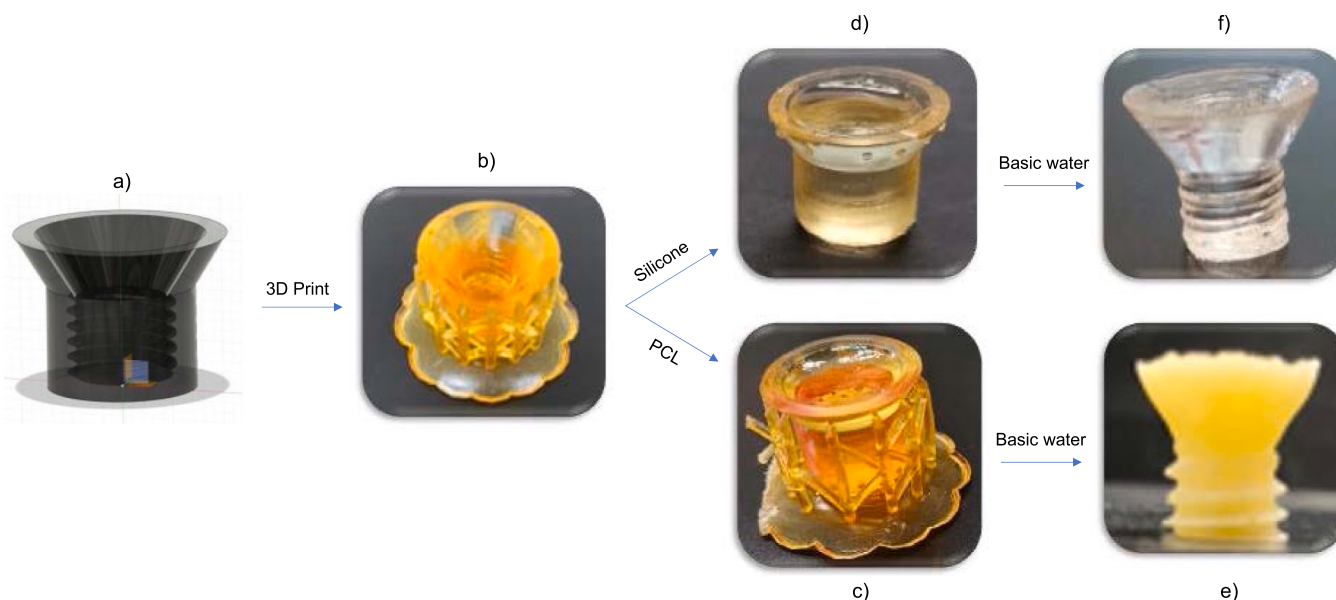


Fig. 10. Scheme of the proof on concept to prepare PCL or silicone screws using the sacrificial molds described in this work. a) Digital design of the mold. b) Printed mold. c) Printed mold filled with the molten PCL (100 °C). d) Printed mold filled with the two components liquid Sylgard 184 (please note that in this case the print support columns have been removed). e) Final PCL screw. f) Final silicone screw.

completely removed in all the explored cases.

This experiment, although a proof-of-concept, highlight the potential of these soluble materials for their use in many different applications were the high resolution of vat photopolymerization 3D printing is required.

4. Conclusions

A direct and scalable route to obtain printable formulations containing hydrolysable crosslinkers has been defined. The 3D printing of these resins, through vat photopolymerization, has given rise in all cases to sacrificial pieces in basic water, that is, soluble, fulfilling the starting hypothesis that sacrificial networks could be obtained using hydrolysable crosslinkers. The versatility of the approach was shown when it comes to intervening in the components of the formulations, which has allowed the properties of the printed parts to be tuned in terms of moduli, stress required for breakage or their elasticity. Thermal resistance up to 180–240 °C has been obtained.

In addition, the strategy has been proven successful for the preparation of versatile sacrificial molds, using them as a mold to be filled with a molten thermoplastic, followed by cooling and solubilization, as well as to be filled with a bicomponent silicone system, followed by chemical crosslinking and solubilization. The templates have shown thermal stability in the PCL range, as well as chemical stability during the chemical crosslinking reaction. These two systems could be evidenced as proofs of concept extensible to other systems, leading to a high potentiality of the product described and evaluated during the work.

CRedit authorship contribution statement

Pedro Liz-Basteiro: Writing – original draft, Methodology, Investigation. **Raúl Sanz-Horta:** Methodology, Conceptualization. **Alberto Gallardo:** Writing – original draft, Supervision, Methodology, Funding acquisition, Conceptualization. **Juan Rodríguez-Hernández:** Writing – original draft, Supervision, Resources, Methodology, Conceptualization. **Enrique Martínez-Campos:** Supervision, Methodology. **Felipe Reviriego:** Validation, Investigation. **Carlos Elvira:** Supervision, Resources, Funding acquisition. **Helmut Reinecke:** Writing – original draft, Methodology, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Alberto Gallardo, Pedro Liz-Basteiro, Raul Sanz-Horta, Felipe Reviriego, Helmut Reinecke, Carlos Elvira, Juan Rodriguez-Hernandez has patent #P202230575 pending to CSIC.

Data Availability

Data will be made available on request.

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Author statement

Formulations have been designed and evaluated for vat photopolymerization 3D printing capable of manufacturing sacrificial parts in

aqueous media, a technology that exists in the lower resolution 3D printing technique of FDM but not in vat photopolymerization.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.addma.2023.103758.

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